

WE CLAIM:

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A porous structured aluminosilicate composition which comprises:

5 a framework of linked tetrahedral SiO_4 and AlO_4 units, the framework defining pores and having an Si to Al molar ratio of between about 1000 to 1 and 1 to 1, and wherein the composition retains at least 50% of an initial framework pore volume after exposure to 20
10 volume % steam at 800°C for two hours.

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A porous structured aluminosilicate composition which comprises:

5 a framework of linked SiO_4 and AlO_4 units, the framework defining pores and having a Si to Al molar ratio of about 1000 to 1 and 1 to 1, and having at least one X-ray diffraction peak between 2 and 100 nm, and wherein the composition retains at least 75% of an initial framework pore volume after exposure to 20
volume percent steam at 600°C for four hours.

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The composition of Claims 1 or 2 assembled from preformed zeolite seeds or zeolite fragments.

The composition of Claims 1 or 2 having a BET surface area of between about 200 and 1400 m² per gram, an average pore size between about 1 and 100 nm and a pore volume of between about 0.1 and 3.5 cm³ per gram.

The composition of Claim 3 wherein the zeolite seeds are formed using a structure director selected from the group consisting of organic onium ions, alkali metal ions and mixtures thereof.

A porous structured aluminosilicate composition which comprises:

5 a framework of linked tetrahedral SiO₄ and AlO₄ units, the framework defining pores having an organic surfactant in the pores and having a Si to Al molar ratio of between 1000 to 1 and 1 to 1 and having at least one X-ray diffraction peak corresponding to a basal spacing between about 2 and 100 nm and wherein the composition is derived from a porogen and preformed
10 zeolite seeds or zeolite fragments.

The composition of Claim 6 wherein the porogen is an organic surfactant is selected from the group consisting of an organic onium ion surfactant and a non-ionic surfactant.

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The composition of Claim 7 wherein the surfactant is a non-ionic surfactant selected from the group consisting of a non-ionic polyethylene oxide surfactant and a non-ionic amine surfactant.

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The composition of Claim 6 wherein the zeolite seeds are formed using a structure director selected from the group consisting of organic onium ions, alkali metal ions and mixtures thereof.

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The composition of Claim 1, 2 or 3 containing between about 0.1 and 50% by weight carbon in the framework pores.

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The composition of Claims 1 and 2 with an infrared absorption band between 500 and 600cm⁻¹.

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The composition of Claim 6 wherein the porogen is an organic surfactant which contains a co-surfactant selected from the group consisting of alkyl alcohol, alkyl amine, aromatic hydrocarbon and mixtures thereof containing between about 2 and 36 carbon atoms in the alkyl and 6 to 36 carbon atoms in the aromatic hydrocarbon.

A process for forming a porous aluminosilicate composition which comprises:

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(a) providing zeolite seeds or zeolite fragments in a form selected from the group consisting of an aqueous solution, gel, suspension wetted powder and mixtures thereof;

(b) mixing in a mixture the zeolite seeds or zeolite fragments in an aqueous medium with an organic porogen;

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(c) aging the mixture of step (b) at a temperature between 25° and 200°C to obtain a precipitate of the composition; and

(d) separating the composition from the mixture of step (c).

The process of Claim 13 wherein the porogen is a surfactant.

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The process of Claim 14 wherein the organic surfactant is selected from the group consisting of onium ion surfactants and non-ionic surfactants.

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5 The process of Claim 13 wherein the porogen is an organic surfactant which contains a co-surfactant selected from the group consisting of alkyl alcohol, alkylamine, aromatic hydrocarbon and mixtures thereof containing between about 2 and 36 carbon atoms in the alkyl and 6 to 36 carbon atoms in the aromatic hydrocarbon.

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The process of Claims 13 or 14 wherein the zeolite seeds are formed using a structure director selected from the group consisting of organic onium ions, alkali metal ions and mixtures thereof.

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The process of Claims 13 or 14 wherein in addition the composition is calcined.

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The process of Claims 13 or 14 wherein in addition the composition is calcined at above about 400°C.

A structured aluminosilicate porous composition which comprises:

5 a framework of linked tetrahedral SiO_4 and AlO_4 units, the framework defining mesopores, having a porogen in the pores of the composition, having an Si to Al molar ratio of between about 1000 to 1 and 1 to 1, and having at least one X-ray diffraction peak corresponding to a basal spacing between about 2.0 and 100 nm, and which when calcined retains at least 50% of an initial framework pore volume after exposure to 20 10 volume % steam at 800°C for two hours.

The composition of Claim 20 wherein the porogen is a surfactant is selected from the group consisting of:

(a) an ammonium or phosphonium ion of the formula $R_1R_2R_3R_4Q^+$, wherein Q is nitrogen or phosphorous, and wherein at least one of the R moieties is selected from the group consisting of aryl, alkyl of between about 6 to 36 carbon atoms and combinations thereof, remaining of the R moieties are selected from the group consisting of hydrogen, alkyl of from 1 to 5 carbon atoms and combinations thereof, and

(b) a non-ionic block surfactant containing polyethylene oxide units in a hydrophilic block and polypropylene oxide, polybutylene oxide, alkyl, or aryl units in a hydrophobic block, and nonionic amine surfactants containing 6 to 36 carbon atoms.

The composition of Claim 20 wherein the porogen is a surfactant and a co-surfactant and the co-surfactant is selected from the group alkyl amine, alkyl alcohol, aromatic hydrocarbon and mixtures thereof, wherein the number of carbon atoms in the co-surfactant is between 2 and 36.

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The composition of any one of Claims 1, 2, 6 or 20 wherein the framework has a structure which is hexagonal, cubic, lamellar, wormhole or cellular foam.

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The composition of Claims 6 or 20 wherein the porogen is removed by calcination, by ion exchange, or by a combination of ion exchange and calcination.

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5 A porous aluminosilicate composition which comprises: a framework of tetrahedral linked SiO_4 and AlO_4 units, the framework defining mesopores having an Si to Al molar ratio of between about 1000 to 1 and 1 to 1, and having at least one X-ray diffraction peak corresponding to a basal spacing between about 2.0 and 100 nm, wherein a BET surface area is between 200 and 1400 m^2 per gram, wherein an average pore size of the framework is between about 1.0 and 100 nm, and wherein 10 a pore volume of the framework is between about 0.1 and 3.5 cm^3 per gram, and which retains at least 50% of an initial framework pore volume after exposure to 20 volume % steam at 800°C for two hours.

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The composition of Claim 25 wherein the framework has a structure which is hexagonal, cubic, lamellar, wormhole, or cellular foam.

A hybrid porous aluminosilicate - carbon composition which comprises: a framework of linked tetrahedral SiO_4 and AlO_4 units, the framework defining mesopores having an Si to Al molar ratio of between 5 about 1000 to 1 and 1 to 1 and between 0.01 and 50 wt% carbon embedded in the mesopores, and having at least one X-ray diffraction peak corresponding to a basal spacing between about 2.0 and 100 nm, wherein a BET surface area is between 100 and 1400 m^2 per gram, 10 wherein an average pore size of the framework is between about 1.0 and 100 nm, and wherein a pore volume of the framework is between about 0.1 and 3.5 cm^3 per gram, and which retains at least 50% of an initial framework pore volume after exposure to 20 volume % steam at 800°C for 15 two hours.

The composition of Claim 27 wherein the framework has a structure which is hexagonal, cubic, lamellar, wormhole, or cellular foam.

A composition prepared by treating the composition of Claim 20 before calcining with an ammonium salt solution at a temperature between about 0° and 200°C for a period of up to 24 hours and repeating the treatment up to ten times to introduce ammonium ions into the composition, collecting and drying the resulting composition, and then calcining the resulting composition at a temperature between about 400 and 900°C to remove the organic porogen and to convert a fraction of the surfactant or other organic porogen to carbon embedded in the mesopores.

A process for forming a porous aluminosilicate composition which comprises:

(a) reacting a sodium silicate solution at basic pH with a sodium aluminate solution at an aluminum to silicon ratio between about 1000 to 1 and 1 to 1 and aging the mixture at 25 to 200°C for periods of up to 48 hours to form zeolite seeds;

(b) mixing the resultant mixture with an organic porogen;

(c) reducing a pH of the mixture obtained from (b) with a protonic acid to obtain a mixture with an OH^- / (Si+Al) ratio in the range of 0.10 to 10;

(d) aging the mixture from step (c) at a temperature between 20 and 200°C to obtain a precipitate of the composition; and

(e) separating the composition from mixture of step (d).

The process of Claim 30 wherein the sodium silicate is prepared by reacting sodium hydroxide with a silicon source selected from the group consisting of a colloidal silica, a fumed silica, a silica gel, a silicon alkoxide and mixtures thereof.

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The process of Claim 30 wherein the sodium aluminate is prepared by reacting sodium hydroxide with an aluminum source selected from the group consisting of a soluble aluminum salt, a cationic aluminum oligomers, an aluminum hydroxide, an aluminum oxide, an aluminum alkoxide and mixtures thereof.

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The process of Claim 30 wherein the organic porogen is a surfactant selected from the group consisting of:

- (a) a alkyl quaternary ammonium surfactant with a hydrophobic segment which contains between 8 to 36 carbon atoms,
- (b) a non-ionic surfactant containing a polyethylene oxide block as a hydrophilic segment, and
- (c) a non-ionic amine surfactant.

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The process of Claim 30 wherein the composition has a ^{27}Al -NMR resonance line exhibiting a chemical shift in the range of 57 to 65 ppm relative to an external reference of 1.0 M aluminum nitrate.

A process for forming a porous aluminosilicate composition which comprises:

(a) providing zeolite seeds or zeolite fragments in a form selected from the group consisting of an aqueous solution, gel, suspension, wet powder, or combination thereof;

(b) reacting the zeolite seeds in the aqueous medium with an organic porogen wherein the solution has an $\text{OH}^-/(\text{Si}+\text{Al})$ ratio in the range of 0.10 to 10;

(c) aging the mixture from step (b) at a temperature between 20 and 200°C to obtain a precipitate of the composition; and

(d) separating the composition from the mixture of step (c).

A catalyst useful for a fluidized bed catalytic cracking (FCC) or hydrocracking of an organic molecule which comprises:

(a) a porous aluminosilicate composition which comprises a framework of linked tetrahedral SiO_4 and AlO_4 units, the framework defining mesopores having an Si to Al molar ratio of between about 1000 to 1 and 1 to 1, wherein a BET surface area is between 200 and 1400 m^2 per gram, wherein an average pore size of the framework is between about 1.0 and 100 nm, and wherein a pore volume of the framework is between about 0.1 and 3.5 cm^3 per gram, and which retains at least 50% of an initial framework pore volume after exposure to 20 volume % steam at 800°C for two hours; and

(b) a binder for the aluminosilicate composition.

A catalyst useful for fluidized bed catalytic cracking (FCC) or hydrocracking of an organic molecule which comprises:

(a) a porous aluminosilicate - carbon composition which comprises a framework of linked tetrahedral SiO_4 and AlO_4 units, the framework defining mesopores having an Si to Al molar ratio of between about 1000 to 1 and 1 to 1 and between 0.01 and 50 wt% carbon embedded in the mesopores, and having at least one X-ray diffraction peak corresponding to a basal spacing between about 2.0 and 100 nm, wherein a BET surface area is between 100 and 1400 m^2 per gram, wherein an average pore size of the framework is between about 1.0 and 100 nm, and wherein a pore volume of the framework is between about 0.1 and 3.5 cm^3 per gram, wherein the carbon content is between 0.01 and 50% by weight, and which retains at least 50% of an initial framework pore volume after exposure to 20 volume % steam at 800°C for two hours; and

(b) a binder for the aluminosilicate-carbon composition.

A process for catalytic reaction of an organic molecule into lower molecular weight components, which comprises:

(a) providing in a reactor a catalytic cracking catalyst which comprises: a porous aluminosilicate composition which comprises a framework of linked tetrahedral SiO_4 and AlO_4 units, the framework defining mesopores having an Si to Al molar ratio of between about 1000 to 1 and 1 to 1, wherein a BET surface area is between 200 and 1400 m^2 per gram, wherein an average pore size of the framework is between about 1.0 and 100 nm, and wherein a pore volume of the framework is between about 0.1 and 3.5 cm^3 per gram; and a binder for the aluminosilicate composition, and which retains at least 50% of an initial framework pore volume after exposure to 20 volume % steam at 800°C for two hours; and

(b) introducing the organic molecule onto the catalyst at temperatures and pressures which cause the reaction of the organic molecule.

A process for reaction of an organic molecule into lower molecular weight components, which comprises:

(a) providing in a reactor a catalytic cracking catalyst which comprises: a porous aluminosilicate - carbon composition which comprises: a framework of tetrahedral linked SiO_4 and AlO_4 units, the framework defining mesopores having an Si to Al molar ratio of between about 1000 to 1 and 1 to 1 and between 0.01 and 50 wt% carbon embedded in the mesopores, and having at least one X-ray diffraction peak corresponding to a basal spacing between about 2.0 and 100 nm,

wherein a BET surface area is between 100 and 1400 m^2 per gram, wherein an average pore size of the framework is between about 1.0 and 100 nm, and wherein a pore volume of the framework is between about 0.1 and 3.5 cm^3 per gram; and a binder for the aluminosilicate-carbon composition, and which retains at least 50% of an initial framework pore volume after exposure to 20 volume % steam at 800°C for two hours; and

(b) introducing the organic molecule onto the catalyst at temperatures and pressures which cause the reaction of the organic molecule into lower molecular weight components.

A catalyst useful for a fluidized bed catalytic cracking (FCC) or hydrocracking of an organic molecule which comprises:

5 (a) a porous structured aluminosilicate composition which comprises:

10 a framework of linked tetrahedral SiO_4 and AlO_4 units, the framework defining pores and having an Si to Al molar ratio of between about 1000 to 1 and 1 to 1, and wherein the composition retains at least 50% of the initial framework pore volume after exposure to 20 volume % steam at 800°C for two hours; and

(b) a binder for the aluminosilicate composition.

A process for reaction of an organic molecule into lower molecular weight components which comprises:

(a) providing a porous structured aluminosilicate composition which comprises:

5 a framework of linked tetrahedral SiO_4 and AlO_4 units, the framework defining pores and having an Si to Al molar ratio of between about 1000 to 1 and 1 to 1, and having at least one X-ray diffraction peak corresponding to a basal spacing between about 1 and 100 nm, and wherein the composition retains 50% of the initial framework pore volume upon exposure to 20 volume percent steam at 800°C for two hours; and

10 15 (b) introducing the organic molecule onto the catalyst at temperatures and pressures which cause the reaction of the organic molecule to produce the lower molecular weight components.

In a catalyzed organic reaction process, the improvement which comprises:

conducting the reaction with a catalyst which is selected from the group consisting of a porous structured aluminosilicate, gallosilicate, titanosilicate and mixtures thereof which catalyst comprises: a framework of linked tetrahedral SiO_4 and AlO_4 , GaO_4 or TiO_4 units, the framework defining pores and having an Si to combined Ga, Ti and Al molar ratio of between about 1000 to 1 and 1 to 1, and having at least one X-ray diffraction peak corresponding to a basal spacing between about 2 and 100 nm, and wherein the composition retains at least 50% of initial framework pore volume after exposure to 20 volume % steam at 600°C for four hours.

A porous structured silicate composition which comprises:

a framework of linked tetrahedral SiO_4 and units selected from the group consisting of AlO_4 units, GaO_4 units, TiO_4 units and mixed units, the framework defining pores and having an Si to combined Ga, Ti and Al molar ratio of between about 1000 to 1 and 1 to 1, and having at least one X-ray diffraction peak corresponding to a basal spacing between about 1 and 100 nm, and wherein the composition retains at least 50% of the initial framework pore volume after exposure to 20 volume percent steam at 600°C for four hours.

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The composition of Claim 43 assembled from preformed nanoclustered seed precursors.

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The composition of Claims 43 or 44 having an X-ray diffraction peak corresponding to a basal spacing between about 2 and 100 nm, a BET surface area of between about 200 and 1400 m² per gram, an average pore size between about 1 and 100 nm and a pore volume of between about 0.1 and 3.5 cm³ per gram.

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The composition of Claim 44 wherein the seed precursors are formed using a structure director selected from the group consisting of organic onium ions, alkali metal ions and mixtures thereof.

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The composition of Claims 1 and 2 with a ²⁷Al NMR chemical shift between about 57 and 65 ppm relative to an external reference of 1.0 M aluminum nitrate.

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The composition of Claim 1 which contains zeolite crystals.

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The composition of Claim 2 which contains zeolite crystals.

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The composition of Claim 6 which contains zeolite crystals.

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The composition of claim 6 wherein the zeolite fragments are derived from zeolite crystals by digesting with a base.

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The composition of Claim 6 wherein the zeolite fragments are derived from a naturally occurring crystalline zeolite.

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The process of Claim 13 wherein seeds are aged to form zeolite crystals in step (a) prior to addition of the organic porogen.

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The process of Claim 13 wherein the zeolite fragments in step (a) are produced by digesting zeolite crystals with a base.

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The process of Claim 13 wherein the zeolite fragments are derived from naturally occurring zeolite crystals.

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The composition of Claim 27 which contains zeolite crystals.

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The catalyst of Claim 36 which contains zeolite crystals.

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The catalyst of Claim 37 which contains zeolite crystals.

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The process of Claim 38 wherein the catalyst contains zeolite seeds.

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The process of Claim 39 wherein the catalyst contains zeolite seeds.

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The catalyst of Claim 40 which contains zeolite crystals.

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The process of Claim 41 wherein the catalyst contains zeolite seeds.

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The reaction of Claim 42 where the catalyst contains zeolite seeds or zeolite fragments.

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The composition of Claim 43 wherein the catalyst contains zeolite seeds or zeolite fragments.

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A process for forming a porous aluminosilicate composition which comprises:

(a) providing zeolite fragments prepared by disrupting the structure of a crystalline aluminosilicate zeolite in a form selected from the group consisting of an aqueous solution, gel, suspension, wetted powder, and mixtures thereof;

(b) mixing in a mixture the zeolite fragments in an aqueous medium with an organic porogen;

(c) aging the mixture of step (b) at a temperature between 25° and 200°C to obtain a precipitate of the composition; and

(d) separating the composition from the mixture of step (c).

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The process of Claim 65 wherein the fragments are formed by disrupting the structure of a synthetic or naturally occurring zeolite.

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The process of Claim 65 or 66 wherein the organic porogen is an organic surfactant selected from the group consisting of onium ion surfactants and non-ionic surfactants.

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The process of Claim 65 wherein the porogen is an organic surfactant which contains a co-surfactant selected from the group consisting of alkyl alcohol, alkylamine, aromatic hydrocarbon and mixtures thereof containing between about 2 and 36 carbon atoms in the alkyl and 6 to 36 carbon atoms in the aromatic hydrocarbon.

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The process of Claim 65 wherein the zeolite fragments are formed by disrupting the structure of a zeolite through treatment with a base or by subjecting the zeolite to ultrasound, grinding, milling or a combination thereof.

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The process of Claim 65 or 66 wherein in addition the composition is calcined.

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The process of Claim 65 or 66 wherein in addition the composition is calcined at above about 400°C.

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The process of Claim 20 wherein the porogen is a non-surfactant.

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The process of Claim 20 wherein the porogen is triethanolamine.

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A product prepared by the process of Claim 65.

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The composition of Claim 1 having at least one x-ray diffraction peak corresponding to a basal spacing of about 2 and 100 nm.

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The composition of Claim 1 having no x-ray diffraction peaks.

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The process of Claim 13 wherein the zeolite fragment is formed from a crystalline zeolite selected from a group consisting of zeolite Y, zeolite X, zeolite ZSM-5, zeolite ZMS-11, zeolite Beta, and zeolite MCM-22.

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The process of Claim 13 wherein the zeolite fragment is formed from MCM-22(P), the precursor of zeolite MCM-22.

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A carbon composition obtained from the composition of any one of Claims 27, 28 or 29, wherein the aluminosilicate component is removed by dissolving in aqueous base or hydrofluoric acid.

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The composition of Claim 6 wherein the porogen is selected from the group consisting of an amine, ethoxylated amine or alkoxyated amine.

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The process of Claim 13 wherein the zeolite fragment is formed from a crystalline zeolite or a crystalline zeolite precursor.

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The composition of Claim 6 wherein the zeolite seeds or fragments are derived from a crystalline aluminosilicate.

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The composition of Claim 82 wherein the crystalline aluminosilicate is a clay.